

Gas Impermeable Glaze for Sealing a Porous Ceramic Surface

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BACKGROUND OF THE INVENTION

The present invention relates generally to materials and methods for glazing and sealing a porous ceramic surface. In particular, the invention relates to a glass-based glaze capable of sealing the ends of a porous alumina (Al_2O_3) ceramic filter tube. This "membrane-support" tube provides mechanical support for a thin film microporous membrane, which is used to separate hydrocarbon gases at high temperatures. The gas impermeable end seal is used to prevent gas from leaking around the ends during gas separation or other filtration processes.

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Porous ceramic filter media are widely used in chemical processing applications, including liquid phase separations, solid/liquid separations, gas separations, contamination control, and membrane reactor applications. Filter media made of ceramics are generally superior to organic or metallic filter media because of their high temperature stability and inherent resistance to chemical attack. The media can take many geometric forms, such as open or closed-end tubes, plates, cylinders, discs, etc.

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Microporous thin film membranes are used in chemical and petroleum refining processes for separating mixtures of gases by size exclusion (i.e., molecular sieves), such as separating various vaporized organic hydrocarbon isomers in a feedstock stream, or separating individual light gas molecules in stream. Amorphous silicon (e.g., solgel) membranes can be used for low temperature gas separations. The membrane's porosity is highly controlled in order to achieve a high flux and high

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separation efficiency. Microporous membranes are typically deposited or crystallized on a macro-porous mechanical support structure, such as on the inside of a macro-porous alumina tube (hereinafter referred to as "porous alumina", without the modifier "macro", for convenience.

5 A gas impervious surface is needed on the ends of the porous ceramic tube to lock the membranes into the flowstream and to prevent the feed gas from bypassing around (i.e., short-circuiting) the internal microporous membrane, which would degrade the overall separation efficiency. At low temperatures, organic materials can be used to seal the porous surface, such as silicone, epoxy, acrylic, or other
10 polymers. However, these organic materials are unsuitable for use at high temperatures, such as > 200 C, at which point they decompose.

High temperature metallic braze alloys that wet ceramics can be used to seal the porous surface. However, high differential thermal stresses can be generated in the ceramic filter due to the large mismatch in the coefficient of thermal expansion (CTE)
15 between the braze alloy (high CTE) and the ceramic (low CTE), leading to cracking and loss of sealing ability.

Commercially available ceramic glazes can be used to make the gas impermeable surface around the edges or ends of a porous ceramic filter. The ceramic glaze can withstand higher temperatures than organic sealants. The
20 ceramic glazes generally have a closer CTE match to the ceramic filter media than metals, which reduces thermal mismatch stresses. However, commercially available glazes typically include low melting point compositions of mixed oxides, for example, Na_2O , K_2O , PbO , and CaO . Use of these mixed oxides makes them unsuitable for use at high temperatures (e.g., 500 C). Also, undesirable elements in these low-
25 temperature ceramic glazes can disassociate and/or diffuse out from the glaze during the subsequent process of depositing or synthesizing the inorganic thin film microporous membrane (e.g., an inorganic zeolite membrane, which is deposited at from 90-200 C). These undesirable elements (or compounds) can interfere with the deposition/synthesis process, poison the membrane, and/or create defects in the
30 microporous structure. These types of glazes also have a lower chemical resistance,

which could partially dissolve in the high pH zeolite crystal-growing bath (the high temperatures used to grow the zeolites would increase the dissolution rate also).

The gas impermeable glaze preferably should be applied prior to growing the thin zeolite film. Because zeolite crystallization generally occurs under basic conditions, at high temperature, and sometimes with organic solvents, the glaze needs to be chemically stable. The glaze should not dissolve and become part of the reaction mixture during zeolite growth, which would interfere with crystal growth rates and affect the zeolite crystal's pore size. Since synthesis of zeolite films can be performed at temperatures as high as 200 C, the glaze should be stable at temperatures greater than 200 C (and, preferably, greater than 500 C for use in hydrocarbon gas separation processes). The glazed coating needs to be sufficiently strong to permit the use of gas-tight, metallic compression-type seals to be made (e.g., Swagelock™ type compression fittings) to the glaze. The glazed coating should be relatively thin, but not so thin as to crack or not provide a 100% "pinhole" free (i.e., < 3 Angstroms) hermetic seal.

A need remains, therefore, for a material and method for glazing and sealing the edges or ends of a porous surface, such as a ceramic filter media, with a material that is gas impervious, can withstand high temperatures, is chemically stable, mechanically strong, relatively thin, and can be applied prior to synthesizing inorganic thin film separation membrane, such as zeolite-based microporous membranes.

Against this background, the present invention was developed.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form part of the specification, illustrate various examples of the present invention and, together with the detailed description, serve to explain the principles of the invention.

Fig. 1 illustrates a schematic cross-section view of an example of a porous ceramic tube with a glass-based glaze end seal, according to the present invention.

Fig. 2 illustrates a schematic cross-section view of an example of a porous ceramic tube with an internal microporous separation membrane, and with a glass-based glaze end seal, according to the present invention.

Fig. 3 illustrates a schematic cross-section view of another example of a porous ceramic tube with a glass-based glaze end seal, according to the present invention.

Fig. 4 illustrates a schematic cross-section view of another example of a porous axisymmetric ceramic body with a glass-based glaze end seal, according to the present invention.

Fig. 5 illustrates a schematic cross-section view of a gas separation assembly including a porous ceramic tube with a microporous separation membrane, coupled to a feed tube by a union coupling.

Fig. 6 illustrates a schematic cross-section view of an example of a gas separation assembly including a porous ceramic tube with a microporous separation membrane and a glass-based glaze end seal, coupled to a feed tube by a union coupling, according to the present invention.

SUMMARY OF THE INVENTION

The present invention relates to a process for fabricating a gas impermeable seal on a porous ceramic surface using a thin, glass-based, pinhole free glaze. The process can be used to fabricate gas impermeable end seals on porous alumina tubes used as filter media. The porous alumina tubes can have an inorganic microporous thin film separation membrane on the inner surface, which can be used for high temperature gas separation processes.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates generally to materials and methods for glazing porous ceramic surfaces. In particular, the invention relates to a glass-based glaze capable of sealing the ends of a porous alumina (Al_2O_3) ceramic filter tube that provides mechanical support for a thin film microporous membrane, which is used to separate hydrocarbon gases at high temperatures. The gas impermeable end seal is used to prevent gas from leaking around the ends during gas separation or other filtration processes.

In the following discussion, reference to a "gas" stream is defined herein to include mixtures of gases, fluids other than gas, including, but not limited to, liquids, mixtures of different liquids, mixtures of liquids and solid particles, liquids with entrained gases, mixtures of gases and solid particles, and any combination thereof.

Fig. 1 illustrates a schematic cross-section view of an example of a porous ceramic tube with a glass-based glaze end seal, according to the present invention. Porous ceramic tube **10** has a continuous, gas impermeable glaze **12** disposed on at least one of its ends. Glaze **12** covers a length = L of the outer surface **16** of tube **10**, the end **14** of tube **10**, and a length = L of the inner surface **18** of tube **10**.

Porous ceramic tube **10** can be made of a variety of ceramic materials, including, but not limited to, high-purity alumina, alpha-alumina, gamma-alumina, industrial grade alumina, cordierite, mullite, silica, spinel, zirconia, zirconium oxide, silicon carbide, beryllium oxide, silicon nitride, graphite, and other refractory oxides. The pores in tube **10** can have a uniform size throughout the wall thickness, or can have a gradation in pore size across the wall. Porous tube **10** can be made of alpha-alumina, having an average pore size of 1-2 microns, and an average porosity of about 35%. Tubes of this type are manufactured by US Filter, Inc. Alpha-alumina tubes can be made having much smaller pores, e.g., 50 angstroms.

Fig. 2 illustrates a schematic cross-section view of another example of a porous ceramic tube with a microporous separation membrane, and with a glass-based glaze end seal, according to the present invention. Porous ceramic tube **10** has a continuous, gas impermeable end seal **12** disposed on at least one of its ends. End seal **12** covers a length = L of the outer surface **16** of tube **10** and the end **14** of tube **10**, but does not cover the inner surface **18** of tube **10**. The inner surface **18** of tube **10** has a microporous separation membrane **20** extending to the end **14** of tube **10**. Microporous separation membrane **20** can be an inorganic zeolite-based membrane.

Fig. 3 illustrates a schematic cross-section view of another example of a porous ceramic tube with a glass-based glaze end seal, according to the present invention. Porous ceramic tube **11** has a closed end **15**, with a continuous, gas impermeable end seal **12** covering the outer surface of closed end **15**.

Fig. 4 illustrates a schematic cross-section view of another example of an axisymmetric porous ceramic body with a glass-based glaze edge seal, according to the present invention. Axisymmetric porous ceramic disc **13** has a continuous, gas impermeable edge seal **12** covering the outer circumference of disc **13**.

Fig. 5 illustrates a schematic cross-section view of a gas separation assembly including a porous ceramic tube with a microporous separation membrane, coupled to a feed tube by a union coupling. Gas separation assembly **30** does not have a gas impermeable end seal. Gas separation assembly **30** is part of a larger gas separation system (not shown) that provides a means for separating a feed stream **40** of feed gas (i.e., feedstock) into a filtrate (e.g., permeate) stream **44** comprising relatively small components (small molecules, atoms, etc.) and an exit gas stream **42** comprising relatively large components (large molecules, hydrocarbon isomers, etc.). Feed gas **40** is carried within tube **34**, which is coupled to porous ceramic tube **10** by a union coupling **32**. Tube **10** can have a microporous separation membrane **20** disposed on its inner surface. Small fractions **44** of feed gas **40** freely pass through the porous wall of tube **10** (i.e., the filter), while the large fractions **42** are blocked and, hence, exit the outlet end of tube **10**.

In Fig. 5, leakage gas stream **46** can pass through the open (unsealed) porous end **14** of tube **10** and exit the surface **16** of tube **10** without having to pass through microporous separation membrane **20**. Alternatively, leakage gas stream **46** can flow into the plenum region **38** located in-between the outside of tube **10** and the inside of union coupling **32**, then flow into the outer surface **16**, around the seal ring **36** through the connected porosity of tube **10**, and exiting back out through surface **16** on the far side of seal ring **36**, also creating a leakage path. In both cases, the lack of a gas impermeable end seal allows leakage gas **46** to bypass flowing through microporous separation membrane **20**, which degrades the overall efficiency of the separation process.

Fig. 6 illustrates a schematic cross-section view of an example of a gas separation assembly including a porous ceramic tube with a microporous separation membrane and a glass-based glaze end seal, coupled to a feed tube by a union coupling, according to the present invention. In this example, porous ceramic

tube **10** has a gas impermeable end seal **12** coating the end **14** of tube **10** and a portion (**L**) of the outer surface **16** of tube **10**. End seal **12** serves to prevent leakage of any gas through the end **14** of tube **10**, or through the outer surface **16**; effectively preventing any gas from bypassing microporous separation membrane **20**.

5 End seal **12** is free of any materials that comprise the microporous separation membrane **20**, therefore providing a smooth surface for compressing seal ring **36** onto. End seal **12** can also provide additional strength to the porous ceramic tube **10** to resist the compressive force of seal ring **36** applied by coupling **32**.

10 Seal ring **36** can comprise a rubber O-ring, or a compliant polymer, such as silicone, for low temperature use. Alternatively, coupling **32** can be joined to end seal **12** with an epoxy adhesive. For high temperature use, seal ring **36** can comprise one or more soft metallic ferrules or gaskets (e.g. annealed copper, gold, silver, etc.) and coupling **32** can comprise a plurality of threaded metallic members that provide a strong compression force on these ferrules for sealing against the
15 outer surface of end seal **12** and tube **34** (e.g., Swagelock™ fittings). Alternatively, coupling **32** can be soldered or brazed onto end seal **12**.

20 End seal **12** comprises a thin, non-porous, crack-free glass film that is able to partially fill in the large exterior pores of tube **10**. The glass film withstands traditional hydrothermal reaction conditions used for growing crystalline inorganic phases (e.g., for membrane **20**). Tube **10** can be made of an alumina material. The glass composition used for end seal **12** is chosen so its coefficient of thermal expansion matches that of alumina. This eliminates cracking in the glass coating, or splaying of the alumina.

25 An example of a glass composition that meets these criteria is Corning, Inc. Glass Code 7052. This is an alkali barium borosilicate glass having a softening point of 712 C, an annealing point of 484 C, a strain point of 440 C, and Coefficient of Thermal Expansion of $47 \times 10^{-6} \text{ C}^{-1}$ from 0 to 300 C, and a density of 2.27 g/cc. A principle commercial use for 7052 glass is for sealing to Kovar. This glass is available in crushed and powdered forms, and in standard US mesh sized from 4
30 through 325. Preferably, the glass particle size is less than 100 microns, and more

preferably less than 50 microns. This glass may have Na_2O , K_2O , or CaO in its composition. Other glass compositions that match the CTE of alumina can be used.

The glass is fused to alumina tube **10** at a sufficiently high temperature and appropriate time to close any pinholes in the glass, and to allow the glass to
5 penetrate the porous alumina slightly (as shown in Fig. 6). Care must be taken not to heat at too high a temperature, or for too long a time, or the glass will sorb too much of the alumina into solution and possibly change the coefficient of thermal expansion of the glass.

The glass composition for end seal **12** is chosen so that the glass is stable to
10 subsequent hydrothermal and thermal processing, and does not poison any of the controlled pore thin film processes. The glass is applied as a powder from a glass+solvent suspension. The amount of glass applied to the alumina tube is controlled by the ratio of glass powder to solvent. The solvent chosen can effect the uniformity of the fired glass film. A uniformly thick film for end seal **12** is required for
15 achieving a high quality hermetic seal with coupling **32** and seal **36**. A clean, dry alumina tube is dipped into the glass+solvent suspension to a depth sufficient to cover the required length, L, of the outside of tube **10**.

The dipping process is similar to slip casting of ceramics. The porous alumina
tube sucks the solvent from the glass+solvent suspension. Glass particles are
20 carried to the surface of the alumina tube and stick to the tube when it is withdrawn. The glass particles are loosely bound to each other electrostatically.

The solvent in the pores of the tube and between the glass particles is removed
by drying. The tube is then heated to a sufficiently high temperature and for the
correct length of time to cause the glass particles to fuse together and flow into the
25 pores of the alumina tube. This can be done in an atmosphere of nitrogen, argon, or even air. Any large pore area of the alumina tube that has been in contact with the glass+solvent slurry will be coated with glass particles because the pores will suck out the solvent in the slurry. As the solvent is drawn inside the outer pores by capillary forces, the viscosity of the glass+solvent coating increases, thereby
30 improving the stability of the glass+solvent coating prior to furnace firing.

The solvent can be chosen from amyl acetate and Fluorinert™. Fluorinert™ is a trademarked family of products manufactured by 3M Inc., and refers to a family of perfluorocarbon fluids that are routinely used as heat transfer media in a variety of industries, including refrigeration, electronics, semiconductor manufacturing and testing, fuel cells, pharmaceutical, chemical, and other industries. Fluorinert™ fluids have a fully fluorinated structure, and are clear, colorless, odorless, and non-flammable. The family of Fluorinert™ fluids has high density, high dielectric strength, low viscosity, low pour point, and a low surface tension. Boiling points range from 30 C to 215 C and pour points range from -25C to -101 C, depending on the specific composition.

Examples of the process for making the glass seal are as follows:

Example #1

1. Mix 25 grams of Corning 7052 glass powder in 50 mls of amyl acetate.
2. Ultrasonically mix until smooth.
3. Dip porous alumina tube (0.4 inch diameter) to desired depth for a few seconds and withdraw. Turn tube around and dip other end. The solution is good for 2 tube coatings (a total of 4 dips) before the solution should be remixed ultrasonically.
4. Dry under heat lamp for about 1 hour to evaporate solvent.
5. Fire the coated tube in a furnace with atmospheric nitrogen to fuse glass particles. Ramp up to 1000 C at a rate of 5 degrees C/minute. Then, hold at 1000 C for 15 minutes. Then, cool at 15 degrees C/minute to room temperature. Hold tube in center when fusing the glass powder.

Example #2

1. Mix 20 grams of Corning 7052 glass powder in 60 mls of Fluorinert™.
2. Ultrasonically mix until smooth.

3. Dip porous alumina tube (0.4 inch diameter) to desired depth for a few seconds and withdraw. Turn tube around and dip other end. The solution is good for 2 tube coatings (a total of 4 dips) before the solution should be remixed ultrasonically.

4. Dry under heat lamp for about 1 hour to evaporate solvent.

5. Fire the coated tube in a furnace with atmospheric nitrogen to fuse glass particles. Ramp up to 1000 C at a rate of 5 degrees C/minute. Then, hold at 1000 C for 15 minutes. Then, cool at 15 degrees C/minute to room temperature. Hold tube in center when fusing the glass powder.

10 Glass end seals prepared by the processes of Example's 1 and 2 were found to be hermetically tight after being mounted in Swagelok™ metal compression fittings and heat treated.

15 In both examples, the gamma-alumina tubes were baked at 100 C in air for two hours prior to coating to dry them. The mixture of glass+Fluorinert does not appear to be as homogeneous or colloidal as the amyl acetate mixture, even with ultrasonic mixing help. The coating appears more uniform with the amyl acetate also. The Fluorinert, however, is easier to mix but the Fluorinert also evaporates more quickly and the coating may be affected more by the temperature of the alumina tubes when they are coated. The high density (1.8-1.9 g/cc) of Fluorinert serves to suspend the glass particles in the slurry. The higher the density of solvent, the slower the settling of the glass particles (density = 2.28 g/cc). Two types of Fluorinert were used that have the highest densities in the family of Fluorinert fluids: FC-42 (1.9 g/cc) and FC-77 (1.8 g/cc).

25 The nonpermeable glass-based glaze produced by using these processes has the following characteristics: (1) high temperature stability, (2) direct application to the porous ceramic substrate, (3) no interference with thin film growth (e.g., zeolite films), and (4) mechanical stability (necessary for tightening of ends into Swagelok™ fittings). The thickness of glass films made by this process are in the range of 0.001-0.005 inches, and most commonly 0.0025 inches.

Glass powder deposited inside of a porous ceramic tube can be removed prior to firing by drying the solvent and then blowing into the end of the tube to dislodge the loosely adhered glass particles.

Methods, other than dipping by hand, for coating a porous ceramic surface with a suspension or slurry of glass particles suspended in a solvent can be used, including: brushing, spraying, spin coating, vacuum pulling, and slip casting. Solvents other than amyl acetate or Fluorinert fluids can be used, such as alcohol, ethanol, propanol, etc. that don't leave any residual contaminants or organics after evaporating.

Application of the glass-based glaze of the present invention to porous ceramic surfaces can be used to create a vacuum-sealed surface on part, or all, of the surface area of the ceramic part. The glass-based glaze of the present invention can also be used to provide a gas impermeable seal on porous sintered KOVAR metal substrates. In principle, the glass-based glaze can be applied to any material that is wet by the molten glass.

The particular examples discussed above are cited to illustrate particular embodiments of the invention. Other applications and embodiments of the apparatus and method of the present invention will become evident to those skilled in the art.

The actual scope of the invention is defined by the claims appended hereto.